Supporting Information

Mechanism of Hydrocarbon Functionalization by an Iodate/Chloride System: The Role of Ester Protection

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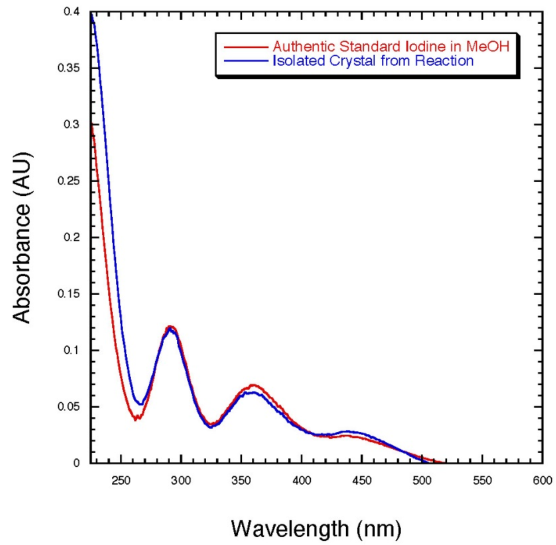

Figure S1. UV-Vis spectra of black crystals formed upon catalytic oxidation of adamantane using NH_4IO_3 and KCl superimposed over the authentic UV-Vis spectrum of iodine.

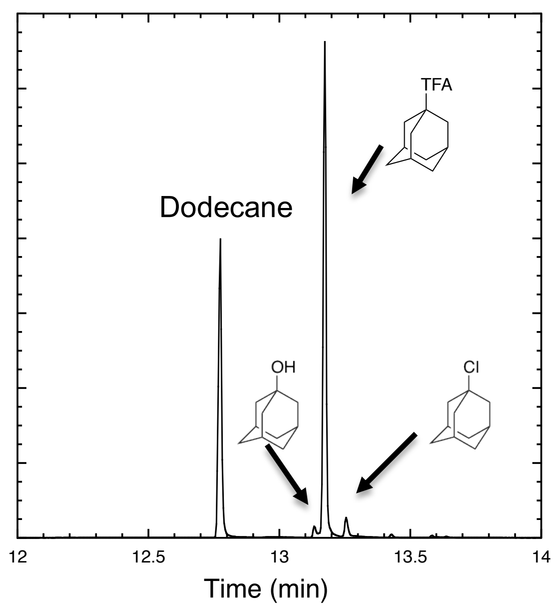

Figure S2. GC-MS trace of adamantane functionalization with KCl/NH_4IO_3 in HTFA. Conditions: Adamantane (1 mmol), KCl (0.15 mmol), NH_4IO_3 (1 mmol) HTFA (4 mL), 100 °C, 1 h. Dodecane (1 mmol) was added as an internal standard after the reaction.

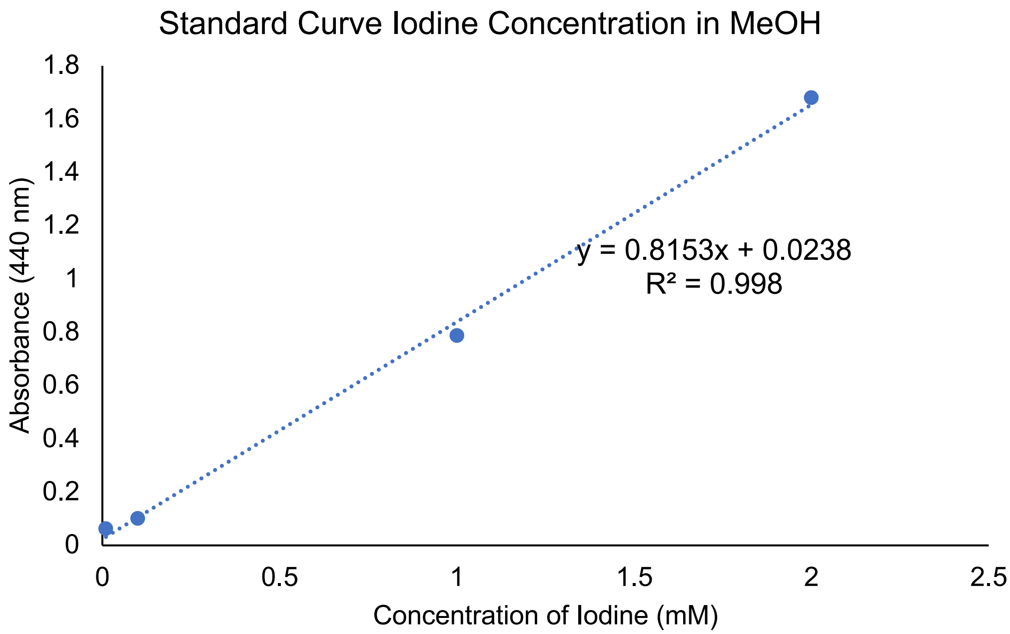

Figure S3. Calibration curve for iodine in methanol by UV-Vis, using the absorbance at 440 nm.

Figure S4. Addition of HTFA to KCl/NH_4IO_3 gives a golden yellow mixture. Conditions: KCl (0.67 mmol), NH_4IO_3 (7.7 mmol), HTFA (8 mL).

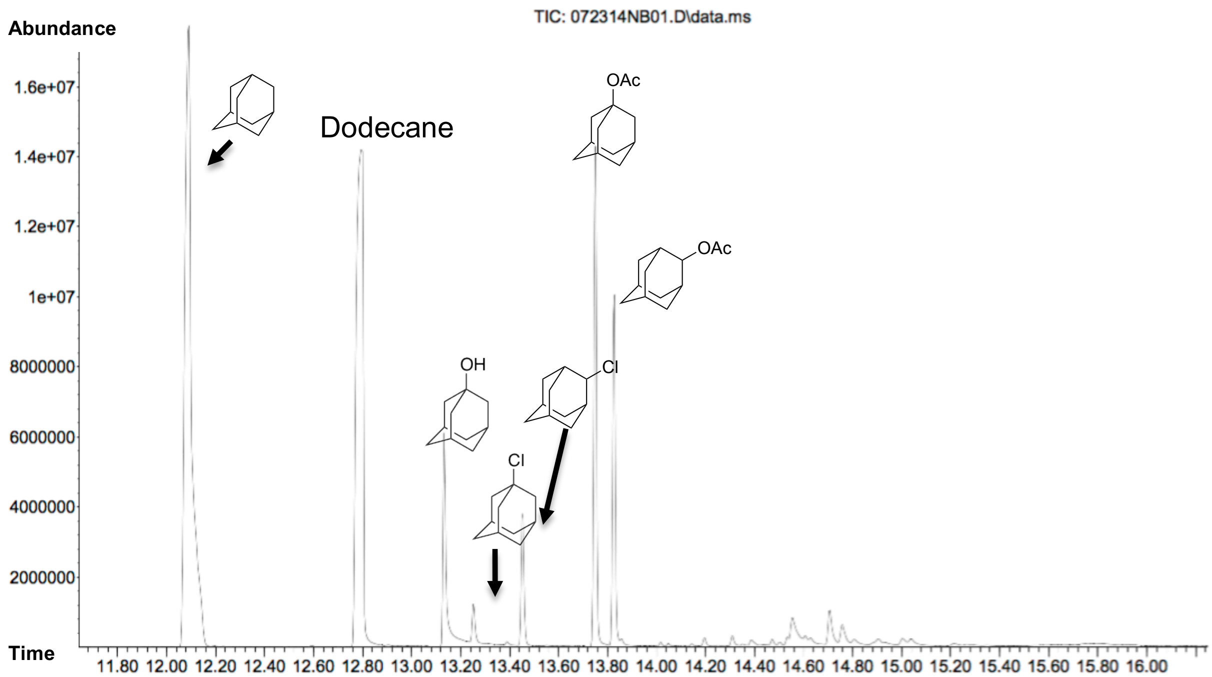

Figure S5. GC-MS trace of adamantane functionalization by KCl/NH_4IO_3 in HOAc. Conditions: Adamantane (1 mmol), KCl (0.15 mmol), NH_4IO_3 (1 mmol), HOAc (4 mL), 180 °C, 1h.

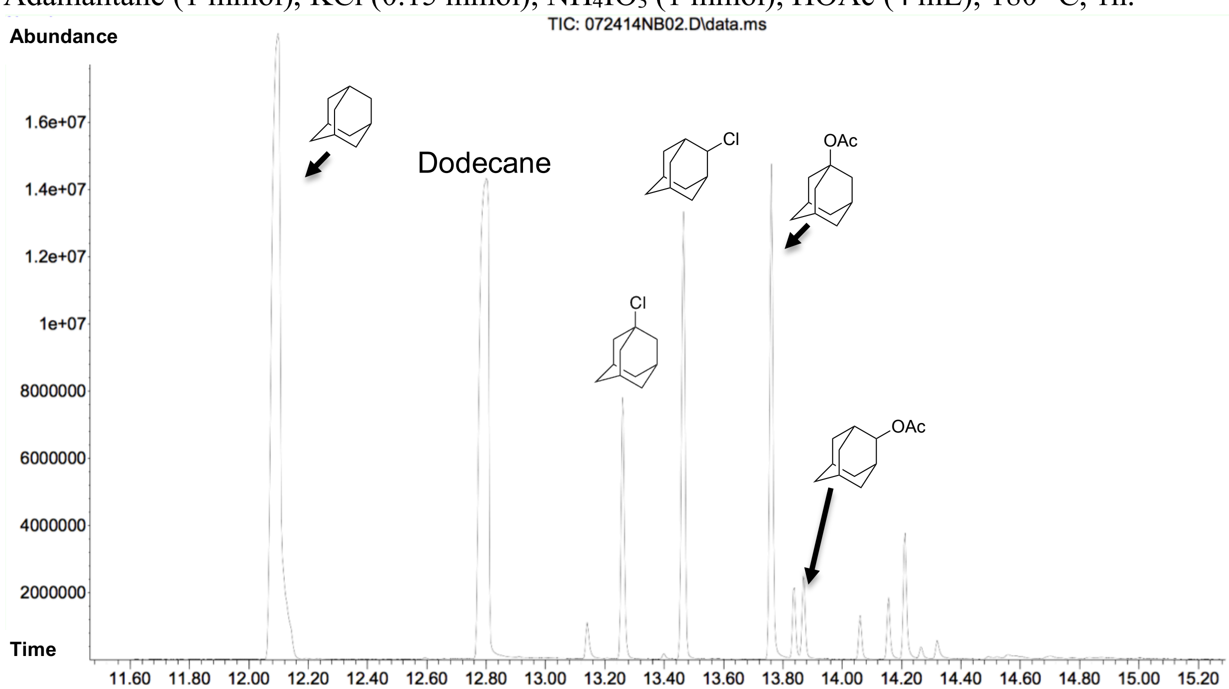

Figure S6. Sample GC-MS trace of adamantane functionalization by *N*-chlorosuccinimide/benzoyl peroxide in HOAc. Conditions: Adamantane (1 mmol), *N*-chlorosuccinimide (0.5 mmol), benzoyl peroxide (0.01 mmol), HOAc (4 mL), 180 °C, 1 h.

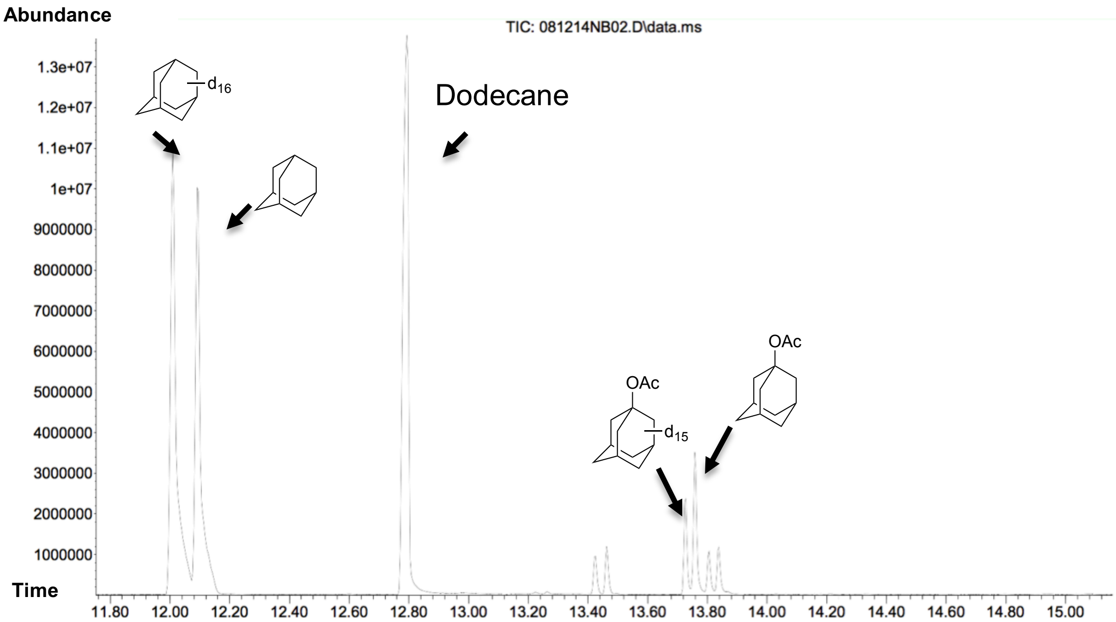

Figure S7. GC-MS trace of adamantane/adamantane-d_{16} (1:1) functionalization by KCl/NH_4IO_3 (1:1) in HOAc. Conditions: Adamantane (0.5 mmol), adamantane-d_{16} (0.5 mmol), KCl (0.15 mmol), NH_4IO_3 (0.2 mmol), HOAc (4 mL), 180 °C, 1 h.

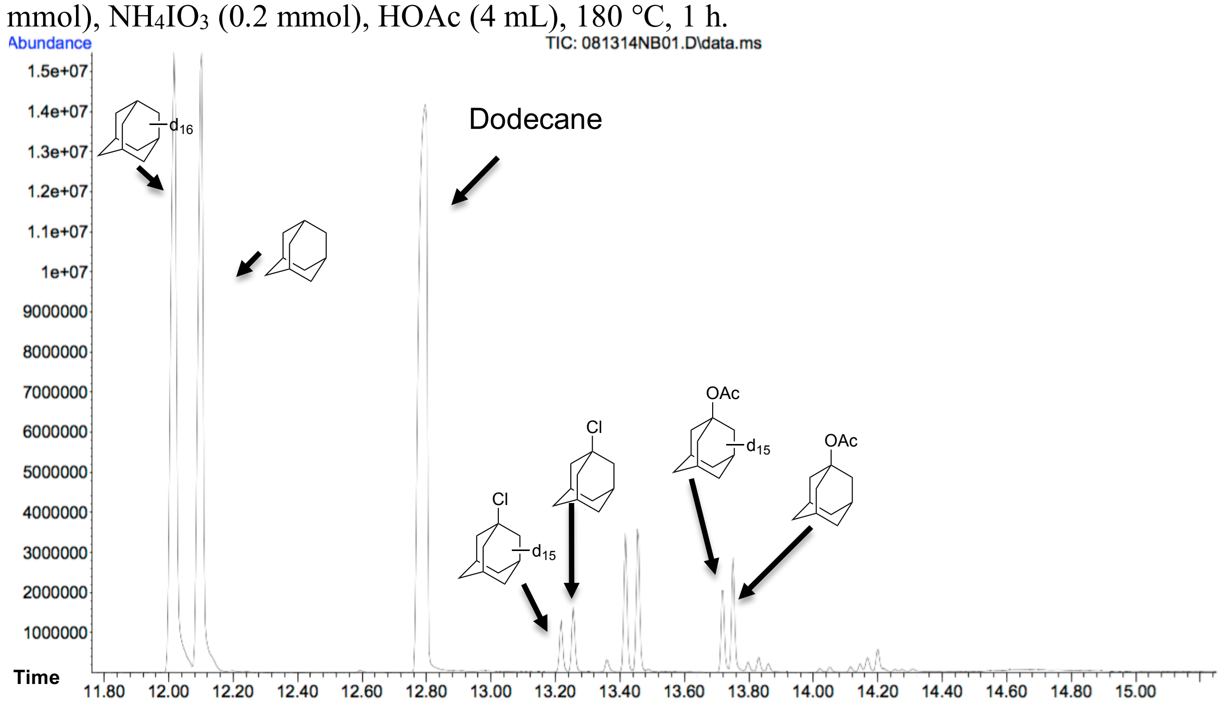

Figure S8. GC-MS trace of adamantane/adamantane-d_{16} (1:1) functionalization by *N*-chlorosuccinimide/benzoyl peroxide in HOAc. Conditions: Adamantane (0.5 mmol), adamantane-d_{16} (0.5 mmol), *N*-chlorosuccinimide (0.2 mmol), benzoyl peroxide (0.01 mmol), HOAc (4 mL), 180 °C, 1 h.

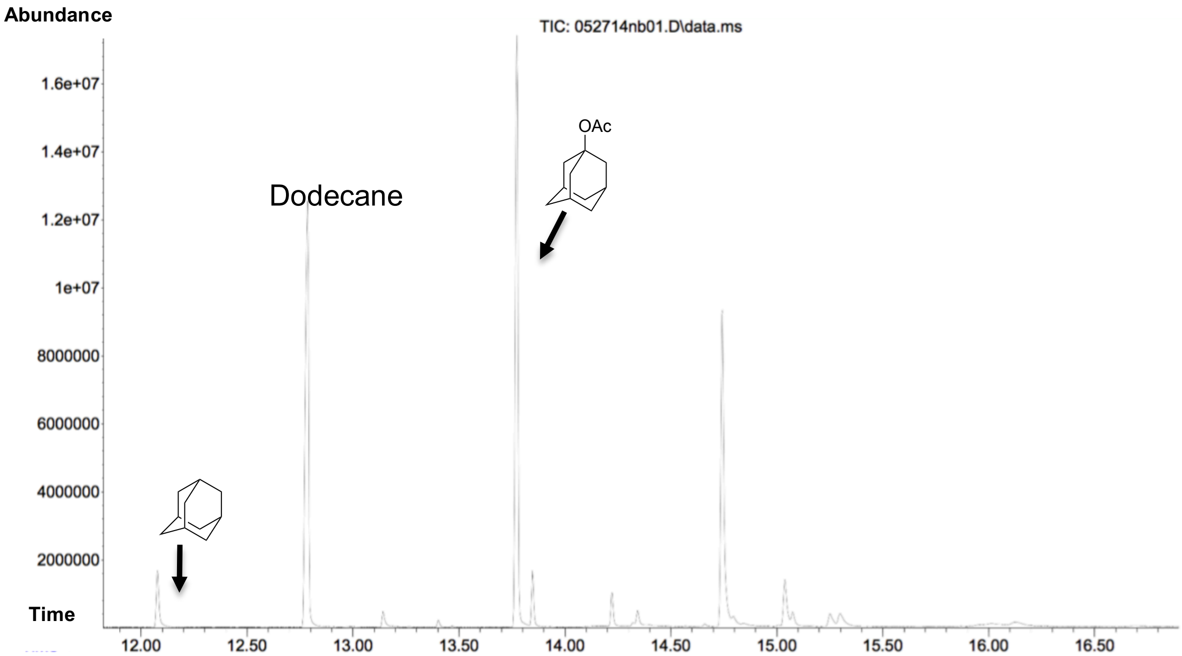

Figure S9. GC-MS trace of adamantane functionalization *N*-hydroxyphthalimide/NH_4IO_3 in HOAc. Conditions: Adamantane (1 mmol), *N*-hydroxyphthalimide (0.15 mmol), NH_4IO_3 (1 mmol), HOAc (4 mL), 180 °C, 1 h.

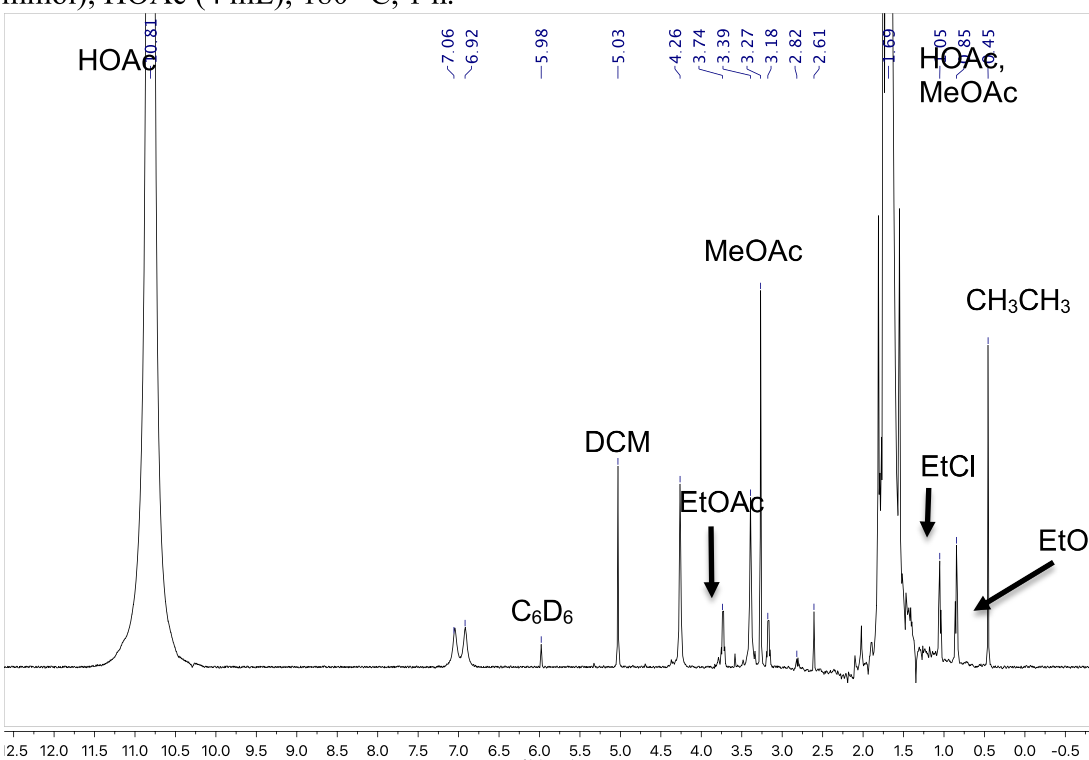

Figure S10. Representative [1]H NMR spectrum of the functionalization of ethane by KCl/NH_4IO_3 in HOAc/Ac_2O. Conditions: Ethane (300 psi, 14.3 mmol), KCl (0.67 mmol), NH_4IO_3 (7.7 mmol), HOAc/Ac_2O (8 mL, 19:1 v:v), 180 °C, 1 h. Dichloromethane (0.469 mmol) was added as an internal standard.

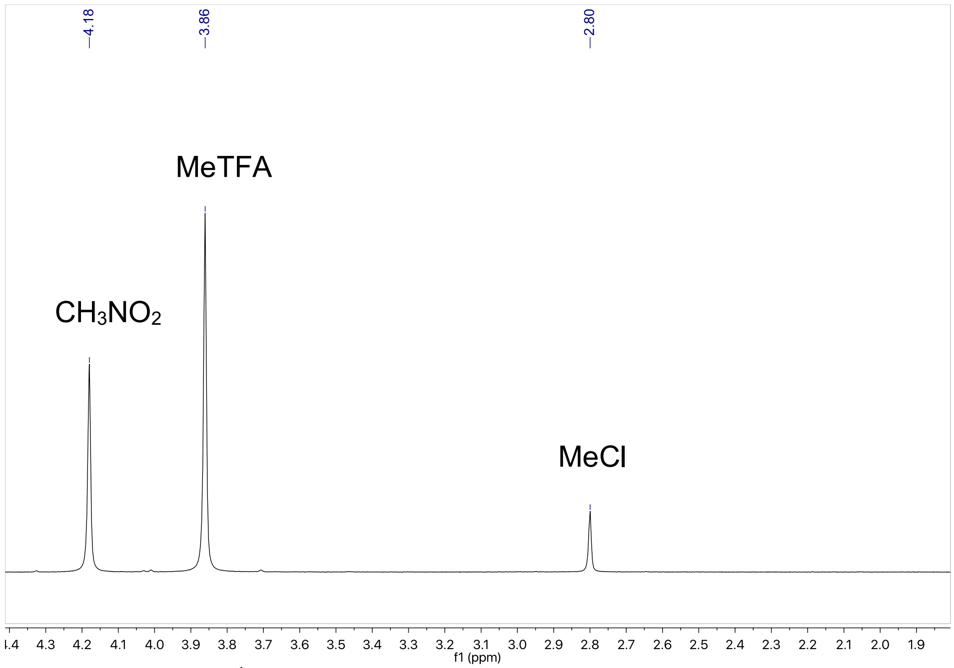

Figure S11. Representative [1]H NMR spectrum of the functionalization of methyl iodide by KCl/NH_4IO_3 in HTFA. Conditions: Argon (100 psi), MeI (1 mmol), KCl (0.67 mmol), NH_4IO_3 (7.7 mmol), 180 °C, 20 min. CH_3NO_2 (0.374 mmol) was added as an internal standard after the reaction. MeI has been fully consumed (MeI resonance: δ 1.91).

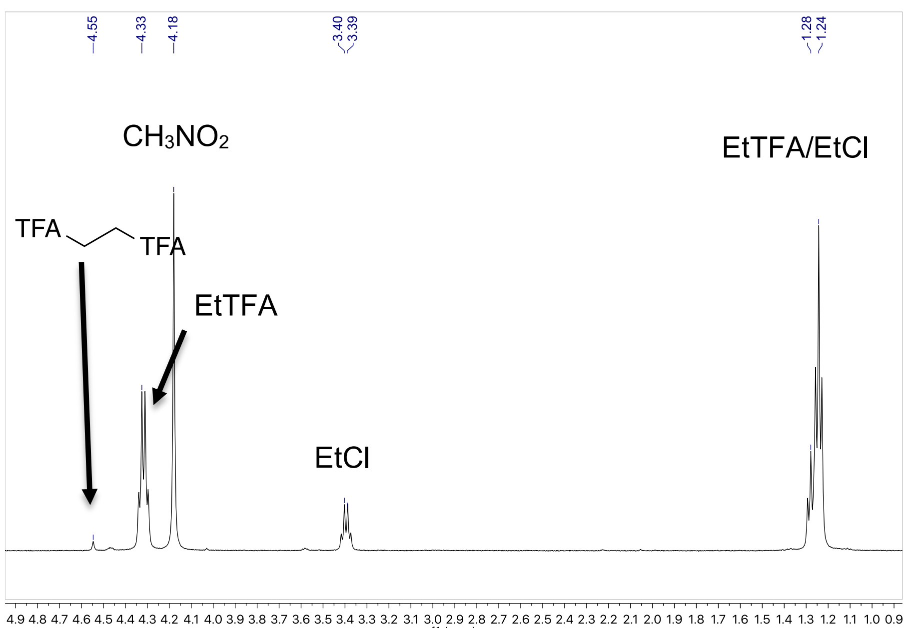

Figure S12. Representative [1]H NMR spectrum of the functionalization of ethyl iodide by KCl/NH_4IO_3 in HTFA. Conditions: Argon (100 psi), EtI (1 mmol), KCl (0.67 mmol), NH_4IO_3 (7.7 mmol), 180 °C, 20 min. CH_3NO_2 (0.374 mmol) was added as an internal standard after the reaction.

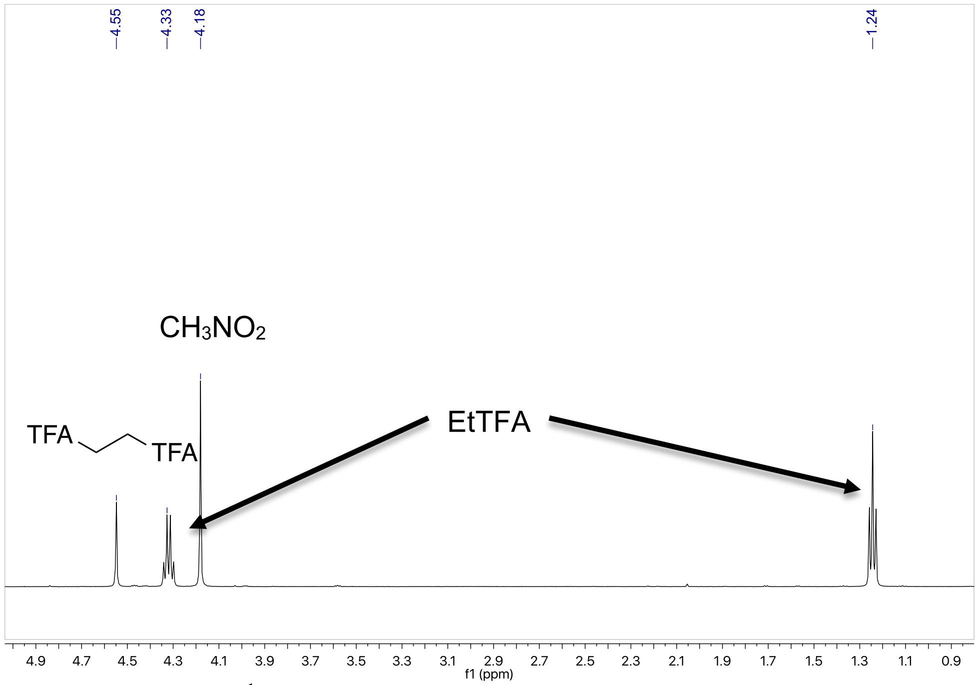

Figure S13. Representative [1]H NMR spectrum of the reaction of ethyl trifluoroacetate with KCl/NH_4IO_3 in HTFA. Conditions: Argon (100 psi), EtTFA (1 mmol), KCl (0.67 mmol), NH_4IO_3 (7.7 mmol), 180 °C, 20 min. CH_3NO_2 (0.374 mmol) was added as an internal standard after the reaction.

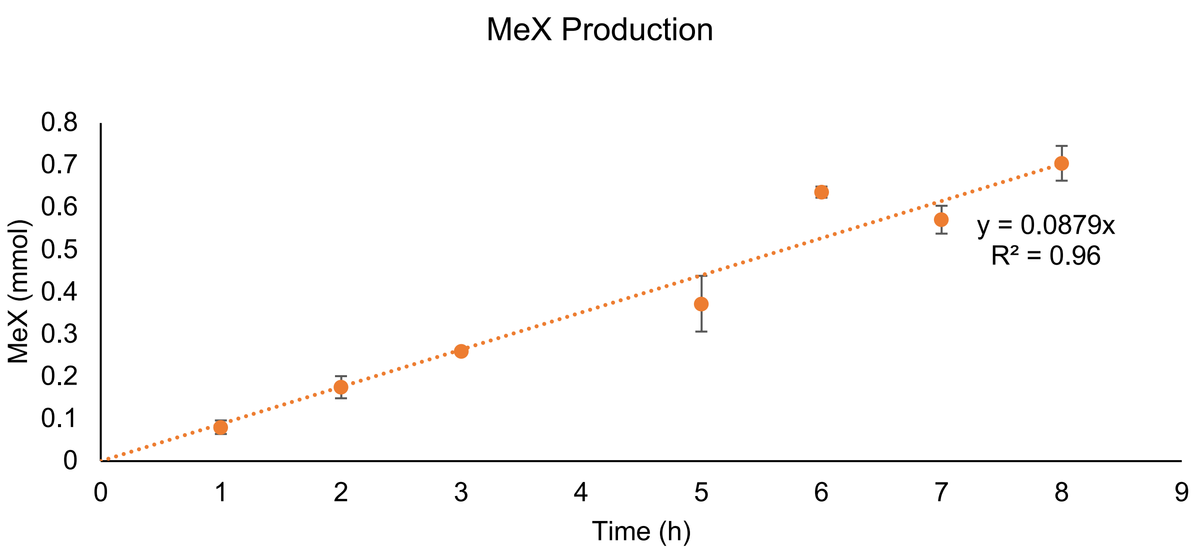

Figure S14. Linear fit of MeX production for the reaction of KCl (0.67 mmol), NH_4IO_3 (7.7 mmol), and HTFA with methane (500 psi) at 140 °C through 8 h.

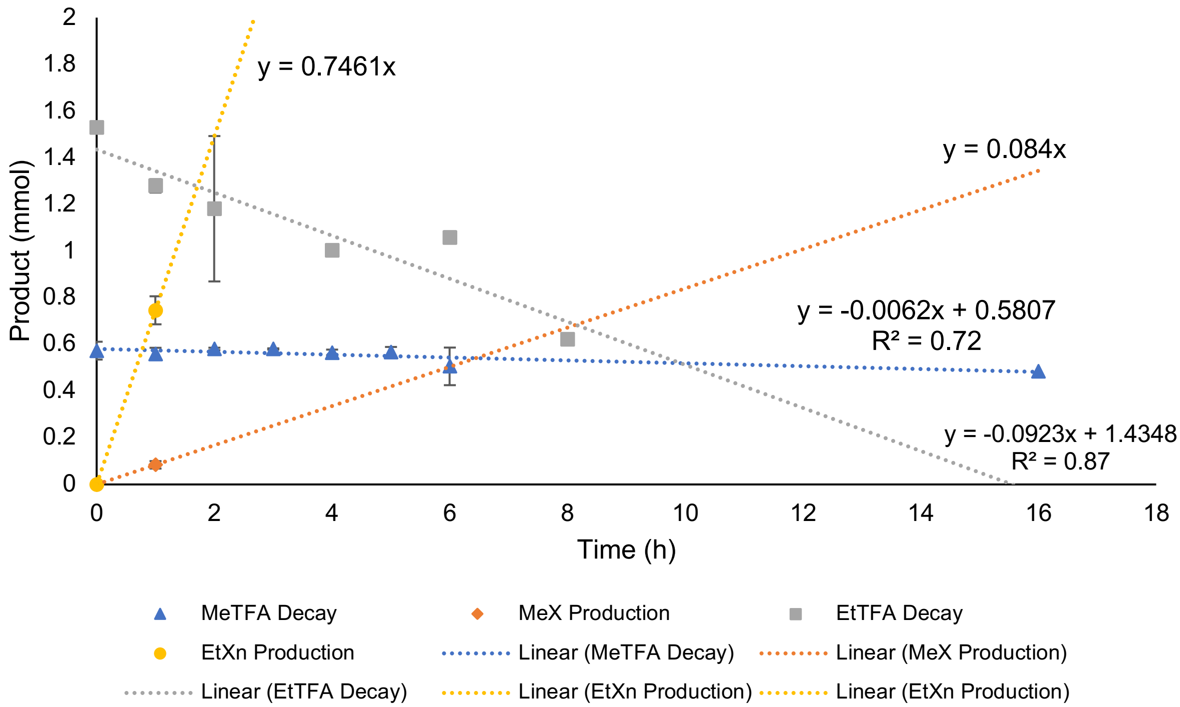

Figure S15. Linear fits for the first data points of MeX (orange) and EtX (yellow) production for the reaction of KCl (0.67 mmol), NH_4IO_3 (7.7 mmol), and HTFA with methane (500 psi) at 140 °C through 8 h. The decay of MeTFA (blue) was tested using MeTFA (0.65 mmol), 500 psi Ar, KCl (0.67 mmol), NH_4IO_3 (7.7 mmol), and HTFA at 140 °C. The decay of EtTFA (gray) was tested using EtTFA (1.51 mmol), 500 psi Ar, KCl (0.67 mmol), NH_4IO_3 (7.7 mmol), and HTFA at 140 °C. Initial amounts of MeTFA and EtTFA for the decay for the plot were determined by setting up controls and taking the ^{1}H NMR immediately to account for loss due to volatility.

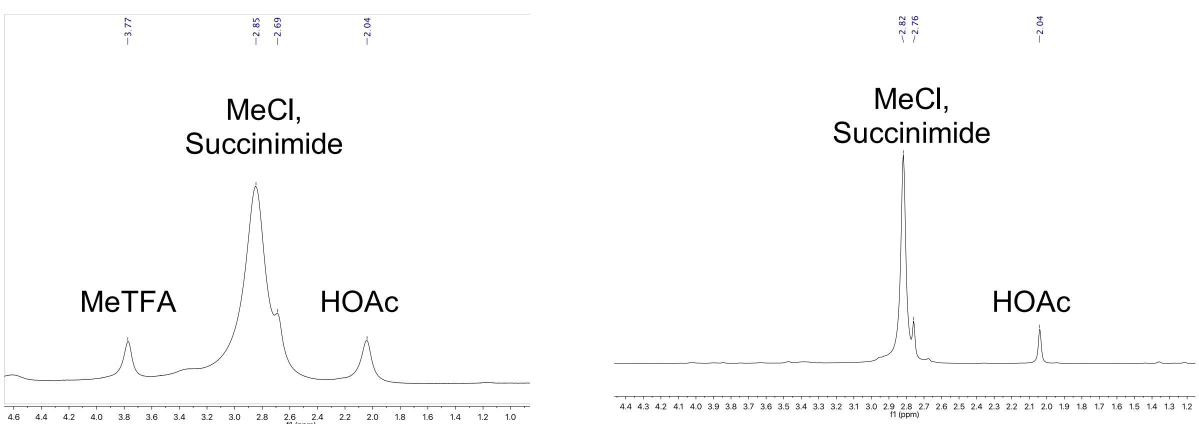

Figure S16. Representative ^{1}H NMR spectrum of the functionalization of methane by *N*-chlorosuccinimide/benzoyl peroxide with (left) and without (right) added iodine. Conditions: Methane (500 psi), *N*-chlorosuccinimide (3.5 mmol), benzoyl peroxide (0.035 mmol), I_2 (left, 0 mmol; right, 0.067 mmol), HTFA (8 mL), 180 °C, 1 h. HOAc (0.35 mmol) was added as an internal standard following the reaction.

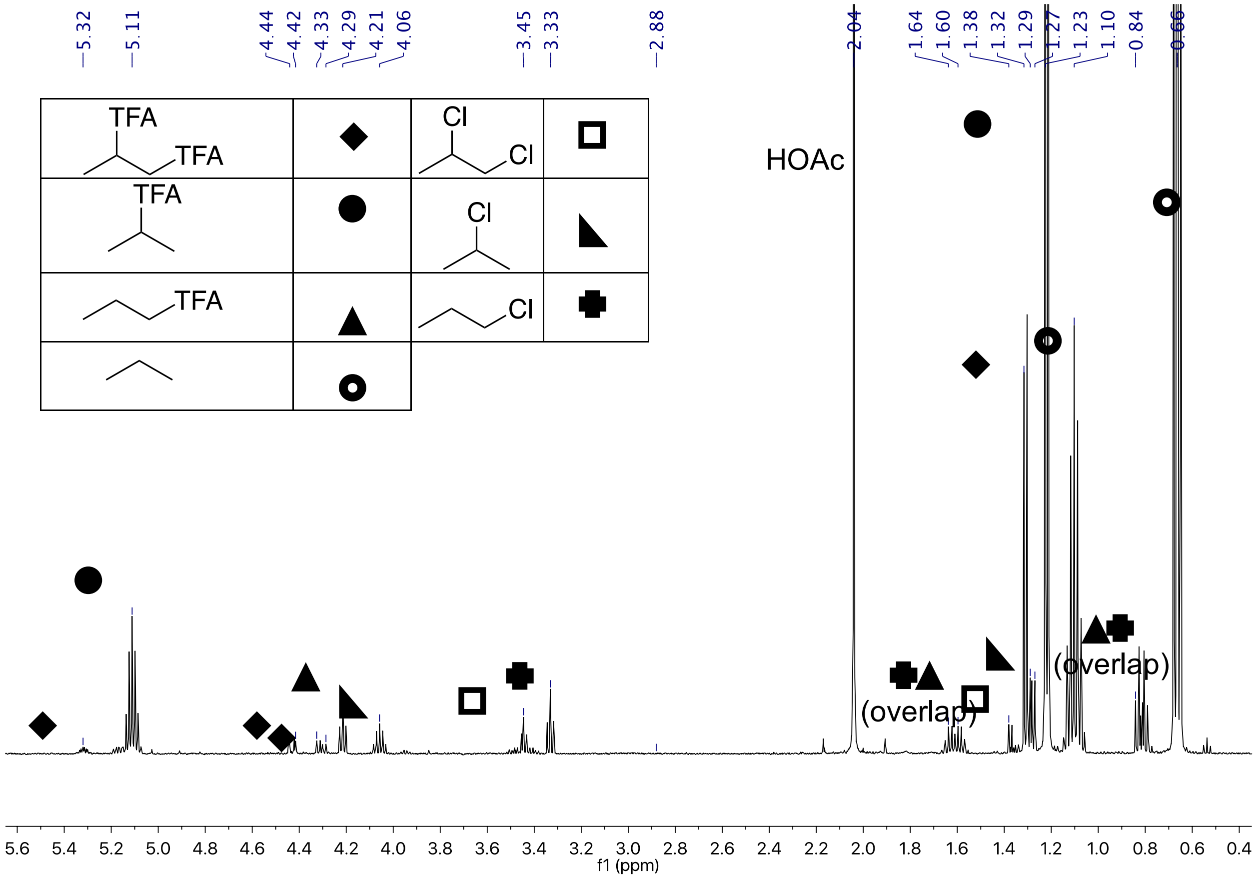

Figure S17. Representative [1]H NMR spectrum of the functionalization of propane by KCl/NH_4IO_3 in HTFA. Conditions: Propane (100 psi, ~9 mmol), KCl (0.67 mmol), NH_4IO_3 (7.7 mmol), HTFA (8 mL), 120 °C, 30 min. HOAc (0.35 mmol) was added as an internal standard following the reaction.

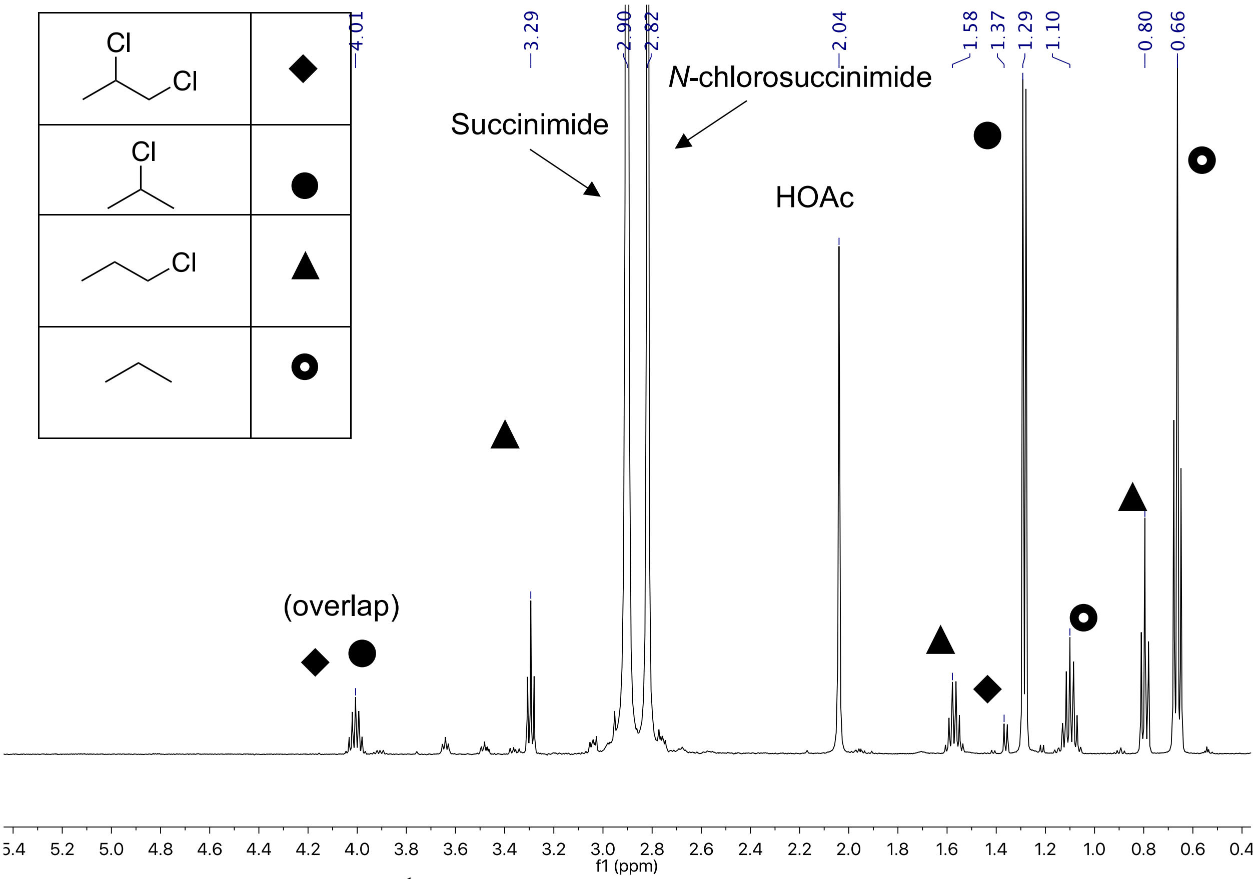

Figure S18. Representative ^{1}H NMR spectrum of the functionalization of propane by *N*-chlorosuccinimide/benzoyl peroxide in HTFA. Conditions: Propane (100 psi, ~ 9 mmol), *N*-chlorosuccinimide (7 mmol), benzoyl peroxide (0.07 mmol), HTFA (8 mL), 120 °C, 30 min. HOAc (0.35 mmol) was added as an internal standard following the reaction.

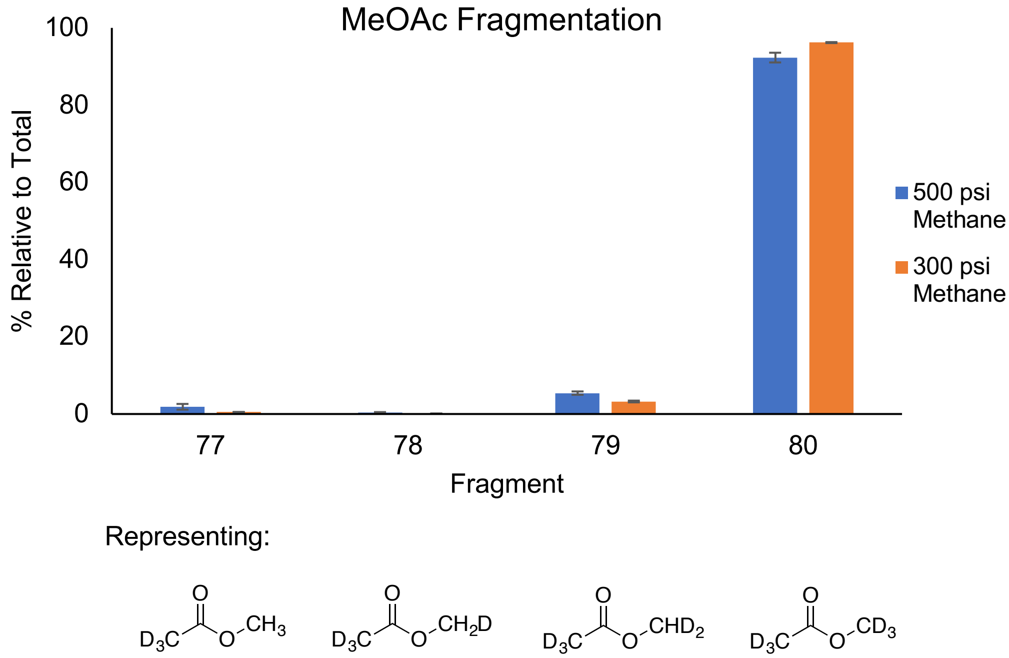

Figure S19. Ratio of m/z for MeOAc from the reaction of perprotio-methane in acetic acid-d_4. Conditions: Methane (300 or 500 psi), KCl (0.12 mmol), NH_4IO_3 (1.44 mmol), acetic acid-d_4 (1.5 mL), 200 °C, 1 h.

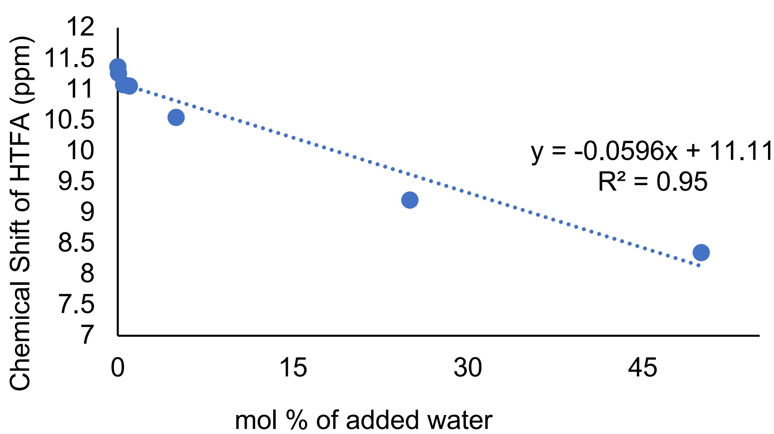

Figure S20. Chemical shift of the HTFA resonance relative to the water content of the mixture with methylene chloride, the internal standard, referenced to 5.03 ppm.